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Identification of the Hydrogeochemical Process in Zahrez Basin, Algeria

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ABSTRACT/RESUME

Abstract: *The Zahrez basin (Fig.1) is one of the endorheic basins of the vast steppes region in the central northern part of Algeria. The Zahrez hydrological basin covers approximately 8,989 km^2. Topography of the area is relatively flat with an elevation ranging from 900 to 1330 meters above mean sea level. The catchment lies between longitudes 2° 15' to 4° 08'E and latitudes 34 35' to 35 30'N. The area is characterized by a semi-arid climate, typically Mediterranean, with an irregular annual rainfall. The mean monthly temperature varies between 3°C and 25°C. The hydrogeochemical processes of groundwater in Zahrez basin were identified based on the combination of geochemical methods, graphical methods, and scatter diagrams. According to the piper diagram, the dominant hydrochemicalfacies in the study area is Ca-Mg-Cl-SO$_4$, which represents 87% of the samples. Mineral saturation indices calculated from major ions, indicate that the groundwater is generally oversaturated with respect to carbonate minerals and undersaturated with respect to evaporite minerals, indicated that the chemical composition of groundwater in the study area is influenced by natural processes of water–rock interaction.*

I. Introduction

The Zahrez basin (Fig.1) is one of the endorheic basins of the vast steppes region in the central northern part of Algeria. The Zahrez hydrological basin covers approximately 8,989 km^2. Topography of the area is relatively flat with an elevation ranging from 900 to 1330 meters above mean sea level. The catchment lies between longitudes 2° 15' to 4° 08'E and latitudes 34° 35' to 35° 30'N [1]. The area is characterized by a semi-arid climate, typically Mediterranean, with an irregular annual rainfall. The mean annual rainfall and potential evapotranspiration are 250 and 1380 mm, respectively, exceeding rainfall for most of the year. The mean monthly temperature varies between 3°C and 25°C. In this region, groundwater is the important source for domestic, agricultural and industrial purposes. Overexploitation of this resource causes a drop in the piezometric level and a progressive degradation of the water quality. Groundwater quality is controlled by natural and anthropogenic factors, such as geological structure, composition of precipitation, geochemical process, the interaction between the groundwater and aquifer minerals, and human activities. The sustainable development of water resources in the arid and semiarid areas highly depends on the investigation of the hydrogeochemical evolution of groundwater [2-3].

II. Materials and methods

II.1. Sampling and analytical methods

During a sampling campaign, performed during October 2011, 47 groundwater samples (Fig. 1)

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were collected from the collected from the Mio-Plio-Quaternary aquifer. Measurements, including temperature, pH, alkalinity (HCO_3), electrical conductivity (EC) and total dissolved were carried out in the field, using the portable Orion EC and pH meters. Water samples were filtered through a 0.45 µm cellulose membrane and collected in 100 ml polyethylene bottles for major and minor element analysis which have been done at the National Agency for Water Resources (ANRH). Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) were analyzed by atomic absorptionspectrometry, anions (Cl^{-}, SO_4^{2-} and NO_3^{-}) by high performance ionic liquid chromatography (HPILC). Bicarbonates (HCO_3^{-}) were determined by acid-base titration method [4, 5].

III. Results and discussion

III.1. Hydrochemicalfacies

The Piper diagram was used to differentiate different water types, based on the basic geochemical character of the constituent ionic concentrations [6]. Therefore the diagram distinguishes types of groundwater as the following (I) Na-K-Cl-SO_4; (II) Na-K-HCO_3; (III) Ca-Mg-HCO_3 and (IV) Ca-Mg-Cl-SO_4. A Piper plot (Fig. 2) of the groundwater chemical data classified the groundwater into the following group of hydrochemicalfacies based on the dominant cations and anions: Na-K-Cl-SO_4 and Ca-Mg-Cl-SO_4. The majority of samples (87%) belonged toCa-Mg-Cl-SO_4.

III.2. Hydrogeochemical processes

Reactions between groundwater and aquifer minerals have a significant role on water quality, which are also useful to understand the genesis of groundwater [7].To identify the origin and processes contributing to groundwater mineralization, some plots of relations between major elements are presented.

III.3. Ionic Relations

The relationships between concentrations of major dissolved elements are shown in Fig. 3.
The Na^{+}–Cl^{-} relationship has often been used to identify the mechanisms for acquiring salinity and saline intrusions in semi-arid regions [8].In the Na versus Cl diagram(Fig. 3a), the majority of samples show a good correlation (R = 0.88), suggesting that the same origin of sodium and chloride is likely related to the halite dissolution. The excess of Cl^{-} can be explained by the combined effect of another source for this ion than the dissolution of halite and the Na^{+} losses due to the phenomenon of base exchange, as clays bedrock can release Ca^{2+} after setting the Na^{+}. The excess of Cl^{-} may also have an anthropogenic origin such as urban wastewater and fertilizers.

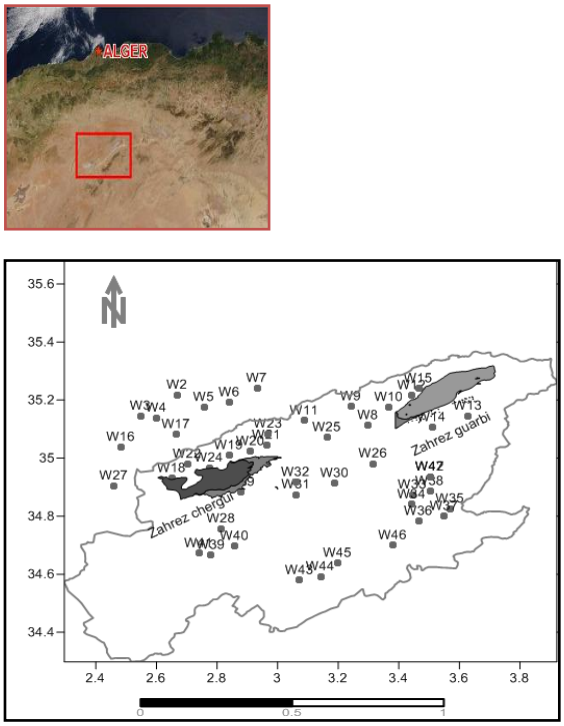

Figure 1. *Sampling map showing the location and numbering of the sampled wells.*

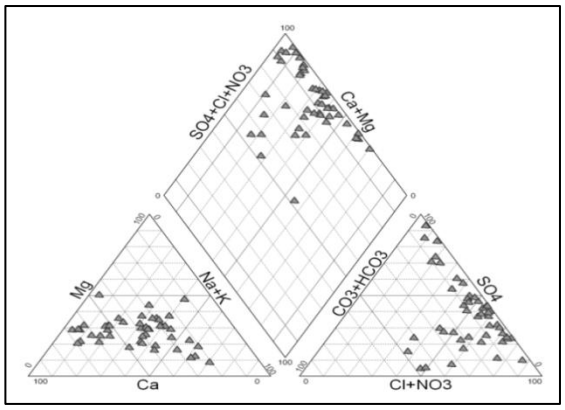

Figure 2. *Piper diagram of groundwater samples in the Zahrez basin.*

The plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^{-} will be close to the 1:1 line if the dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system. Ion exchange tends to shift the points to right due to an excess of SO_4^{2-} + HCO_3^{-}. If reverse ion exchange is the dominant process, it will shift the points to the left due to a large excess of Ca^{2+} + Mg^{2+} over SO_4^{2-} + HCO_3^{-} [9]. The plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^{-}(Fig. 3b) shows that most of the points in this study are plotted on or above the 1:1 line, suggesting that the dissolution of minerals (calcite, dolomite and gypsum) and

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reverse ion exchange are the dominant geochemical processes in the study area. Figure3c shows a scatter plot of Ca^{2+} against SO_4^{2-} concentrations. This plot shows that there are almost 50:50 distributions of the samples above and below the 1:1 trend line. Although some points lie next to that line, showing that both calcium and sulphateare derived from the same origin, which is the dissolution of gypsum and anhydrite, frequently found in the Quaternary formations. The plot of Ca^{2+} + Mg^{2+} vs. Cl^-(Fig. 3d) indicates that Ca and Mg increase withincreasing salinity. In addition, there is a good correlation between these ions (R = 0.81).

III.4. Gibbs Plot

The mechanism controlling chemical relationship of groundwaters based on aquifer lithology was proposed the Gibbs (1970)diagram which is having three fields namely precipitation dominance, evaporation dominance and rock water dominance[10].Gibbs's diagrams representing the ratios of Na^+/Na^++Ca^{2+} and $Cl^-/(Cl^-+HCO_3^-)$ as a function of TDS. Based on the Gibbs diagram (Fig. 4), around 70% of the samples fall under the evaporation dominance category and 30 % samples plotted on rock dominancezone,which suggests that the weathering of rocks controls the major ion chemistry of groundwater in this group. The study area experiences dry and semiarid climatic condition so that evaporation contribute in water chemistry.

III.5. Ion exchange: chloro alkaline indices

The process of cation exchange between groundwater and its host environment is highlighted, by the calculated Base Exchange Indices, in particular the Chloro Alkaline Indices (CAI 1,2) [11].These above indices are calculated using the following equations:

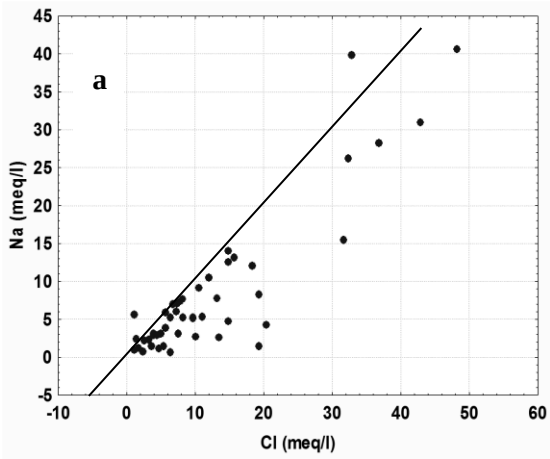
$$\mathrm{CA1} = [\mathrm{Cl} - (\mathrm{Na} + \mathrm{k})]/\mathrm{Cl} \quad \textbf{(1)}$$

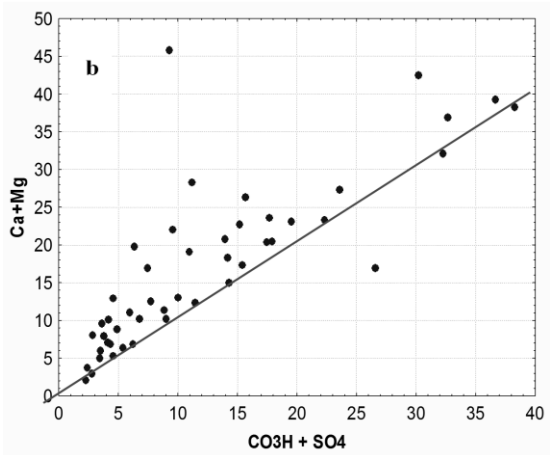
$$\mathrm{CA2} = [\mathrm{Cl} - (\mathrm{Na} + \mathrm{k})]/SO_4 + HCO_3 + NO_3 \quad \textbf{(2)}$$

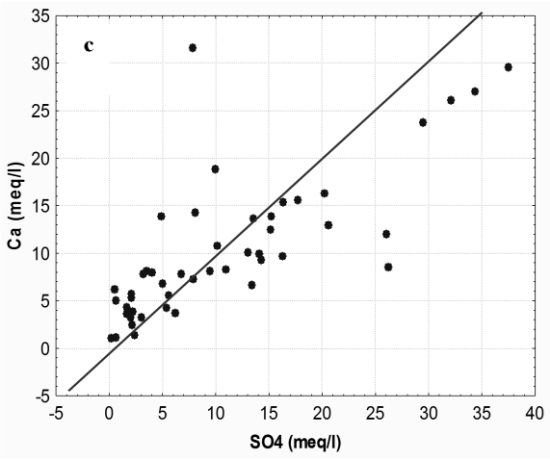
all values expressed in meq/l

When there is an exchange between Na or K in ground-water with Mg or Ca in the aquifer material, both of the indices are positive, indicating reverse ion exchange.

If the exchange takes place between the Ca or Mg in ground-water with Na or K in the aquifer material, the indices will be negative, indicating ion exchange [12].







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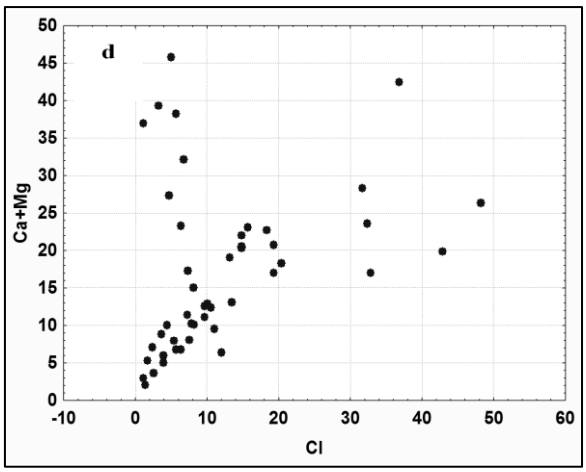

Figure 3. *Major ion relationship: Na^+ versus Cl^- (a), $Ca^{2+}+Mg^{2+}$ and $HCO_3^-+SO_4^{2-}$ (b), Ca^{2+} versus SO_4^{2-} (c), $Ca^{2+}+Mg^{2+}$ and Cl^- (d),*

Figure 5 shows that the groundwater samples have positive values for both indices, which indicate a direct base exchange reaction,which means that Na^+ and K^+ in the water are exchanged with Ca^{2+} and Mg^{2+} in the minerals from the host rock.This explains the reason for the abundance of alkaline earth elements over alkalies in the groundwater.

III.6. Saturation Index (SI)

Saturation indices of minerals are very useful for evaluating the extent to which water chemistry is controlled by equilibrium with solid phases[13]. PHREEQC was used to calculate the saturation indices of groundwater samples with respect to evaporite (gypsum, anhydrite, and halite) and carbonate (calcite, dolomite, and aragonite) minerals via the following equation:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad \textbf{(3)}$$

where IAP and K_{SP} are ion activity product and solubility product constant of minerals at the sample temperature, respectively. In fact, water saturation states for minerals as anhydrite (SI anh.), gypsum (SI gyp.), halite (SI hal.), calcite (SI cal.) and dolomite (SI dol.) were computed. If the SI is < 0, dissolution is considered as the dominant process for the related miner al and when the SI is > 0, precipitation of the mineral is likely to be occurring in the system [14]. Figure 6 shows the saturation indices of halite, (gypsum and anhydrite), (calcite and aragonite) and dolomite, as a function of (Na^+ + Cl^-), ($Ca^{2+}+SO_4^{2-}$), and ($Ca^{2+}+Mg^{2+}+HCO_3^-$), respectively.

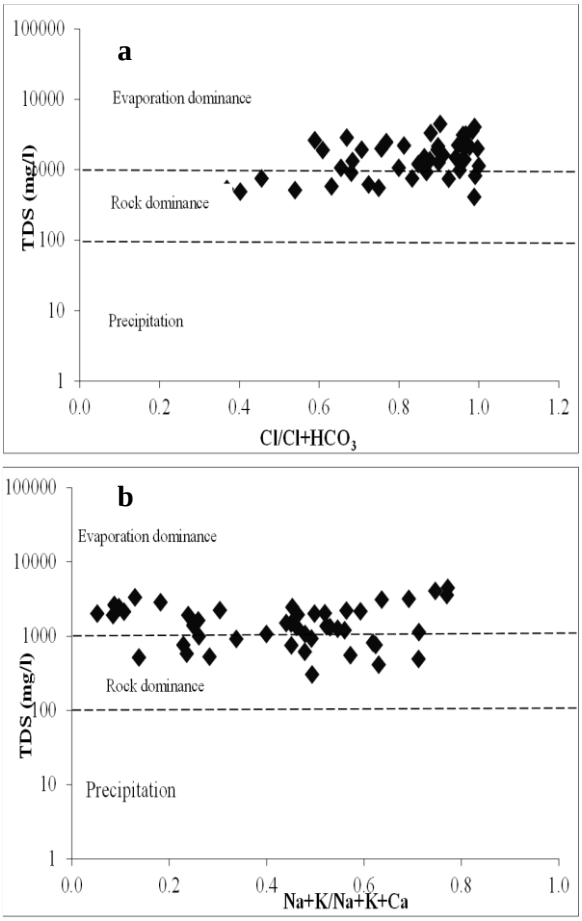

Figure 4. *Gibbs plots explain groundwater chemistry and geochemical process in the study area.*

The plot of SI_{Gypsum} and $SI_{Anhydrite}$vs (Ca + SO_4) exhibits a proportional and parabolic shape evolution with negative values of the saturation indices (Fig. 6a and Fig. 6b). The dissolution of gypsum and anhydrite is also confirmed by the low saturation indices with respect to these minerals (from -3.03 to -0.03 and from -3.25 to -0.24, respectively). Moreover, Halite dissolution is also confirmed by the large negative saturation indices with respect to this mineral (from -7.6 to -4.5), which display proportional and parabolic correlation when represented as a function of Na +Cl values (Fig. 6c).

Calculations showed that carbonate minerals have different degrees of saturation. The calcite SI ranges from -1.4 to 1.86(Fig. 6d),that of aragonite ranges from -0.53 to 1.72 (Fig. 6e), and dolomite SI ranges from -0.71 to 3.51(Fig. 6f).Almost all the groundwater samples are oversaturated with respect to calcite, aragonite, and dolomite, suggesting that these waters tend to precipitate carbonate minerals.

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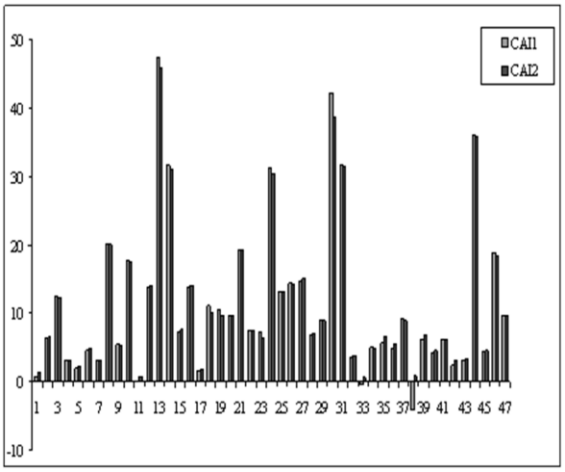
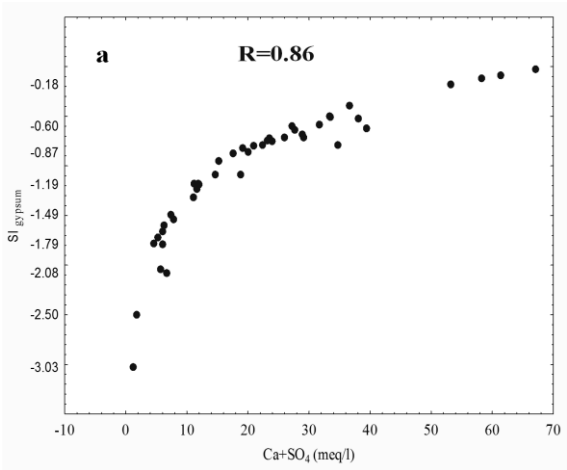
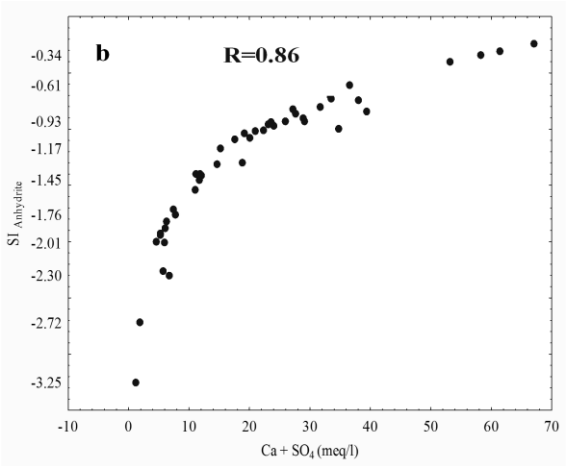
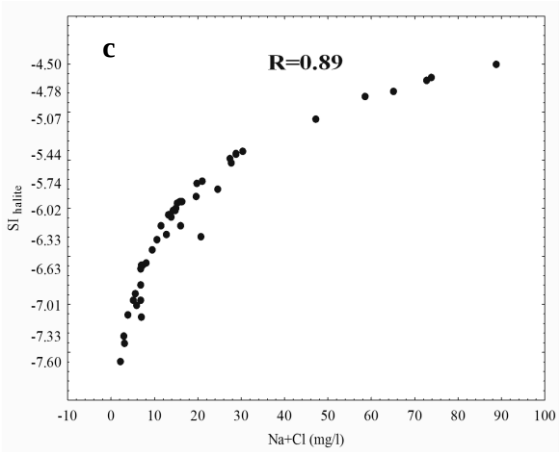
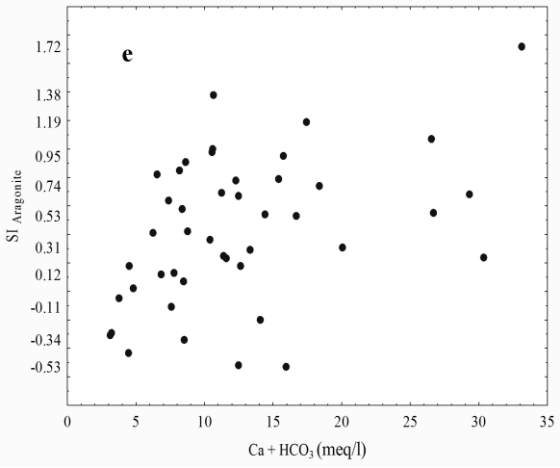


Figure 5. *CAI 1 and CAI 2 of groundwater samples*









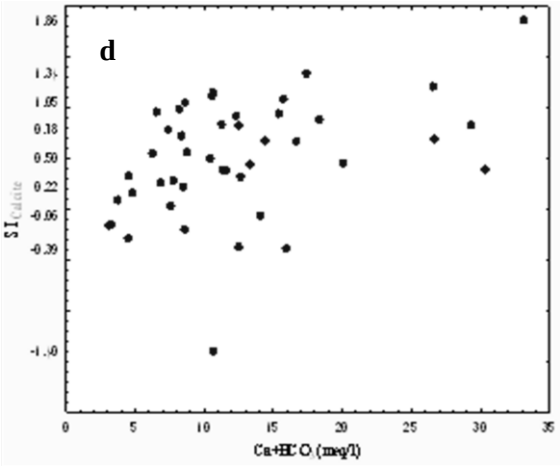


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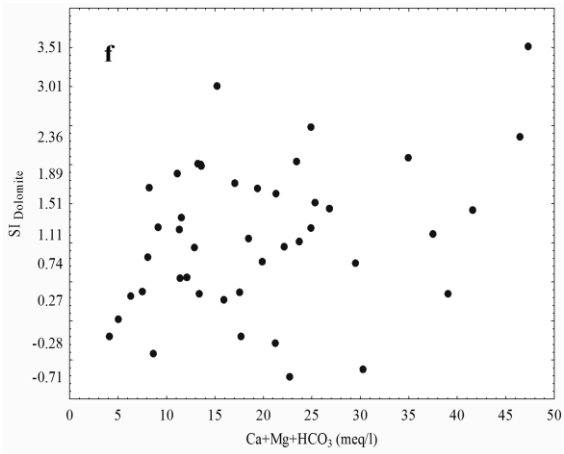
Figure 6. *Gypsum SI versus* $Ca^{2+}+SO_4^{2-}$ ***(a)****, anhydrite SI versus* $Ca^{2+}+SO_4^{2-}$ ***(b)****, halite SI versus* $Na^{+}+Cl^{-}$ ***(c)****, calcite SI versus* $Ca^{2+}+Mg^{2+}+HCO_3^{-}$ ***(d)****, aragonite SI versus* $Ca^{2+}+Mg^{2+}+HCO_3^{-}$ ***(e)****, and*



dolomite SI versus $Ca^{2+}+Mg^{2+}+HCO_3^{-}$ ***(f)*** *relationships of the analyzed water samples.*

IV. Conclusions

The hydrogeochemical analysis reveals that major ion constituents were of the following order: Cl> SO_4> HCO_3 and Ca> Na >Mg > K. According to the piper diagram, the dominant hydrochemical facies in the study area is Ca-Mg-Cl-SO_4, which represents 87% of the samples. Mineral saturation indices calculated from major ions, indicate that the groundwater is generally oversaturated with respect to carbonate minerals and undersaturated with respect to evaporite minerals, indicated that the chemical composition of groundwater in the study area is influenced by natural processes of water–rock interaction such as dissolution of evaporitic rocks (gypsum, anhydrite, and halite). Finally, the results of this study helped to significantly improve the understanding of the hydrogeochemical processes controlling groundwater chemistry in Zahrez basin.

V. References

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